# HIGH TEMPERATURE MASS SPECTROSCOPY OF ATHABASCA ASPHALTENES AND THE RELATIONSHIP TO CRACKING PROCESSES

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## INTRODUCTION

In a previous communication (1), it was shown that Athabasca asphaltenes are composed predominantly of peri-condensed aromatic systems, varying from six to fourteen rings per sheet, bearing alkyl and naphthene substituents. The present paper represents a further facet of a systematic investigation into the properties and potential uses of the Athabasca bitumen and fractions arising therefrom. More particularly, the work described herein is a preliminary attempt to elucidate the predominant mechanisms involved in the cracking of asphaltenes. The thermal treatment of Athabasca bitumen has been the subject of several earlier publications. For example, Ball (2) described the bitumen in general terms as being susceptible to heat and, therefore, to refining processes; Peterson and Gishler (3) investigated the recovery of oil from the bituminous sand by feeding the sand directly into a hot fluidized bed; Krieble and Seyer (4) investigated the fractional distillation of the oil at reduced pressures; Pasternack (5-7) studied the partial thermal cracking of the bitumen and noted changes in such properties as molecular weight and carbon residue of the bitumen; Erdman and Dickie (8) noted the changes in viscosity and density during the mild thermal alteration of the bitumen; and McNab and his co-workers (9) calculated activation energies for cracking of the bitumen and concluded that the bitumen was more thermally labile than a conventional crude oil.

## EXPERIMENTAL

### Materials and General Techniques

The asphaltene fraction was isolated by diluting dry Athabasca bitumen with 40 volumes of technical pentane (containing 93% n-pentane), followed by agitation of the mixture for not less than 5 hours. The asphaltenes were separated by filtration and washed thoroughly with fresh portions of pentane until the washings were colourless and evaporation of an aliquot failed to leave any residue.

### Cracking Procedure

The apparatus consisted of standard Pyrex glass equipment fitted with B14/23 ground glass joints. The asphaltenes (50.0 $\pm$ 0.2 g) were cracked in a round-bottomed flask (100 ml capacity) which was heated by an alloy bath. Products passed through an air-cooled condenser

(25.4 cm long) and liquids were collected in a water-cooled receiver. Gases were collected in a series of traps cooled to -78°C, -130°C, and -196°C which were protected from the atmosphere by a mercury lock attached to the -196°C trap. In order to commence distillation, the apparatus was flushed with dry helium (75 ml/min) for five minutes whilst the temperature was raised to 200°C. The helium flow was discontinued and the temperature was then (a) in one experiment, raised rapidly to 455°C over fifteen minutes and maintained there for two hours by which time all of the distillate had been collected, (b) in a separate experiment, raised to 455°C over a period of two hours by which time distillation was complete.

At the end of each distillation, the distillate was raised, in situ, to 150°C for one hour to remove any dissolved gases. Spectroscopic and physical examination prior to and after the thermal treatment indicated no change to the distillate itself.

The residues were insoluble honeycombed coke-like materials from which small amounts of resinous materials could be extracted with benzene during 24 hours. The insoluble coke had no appreciable absorption in the infrared. For convenience, the products from these distillations are designated as oil, resins, and coke.

The proportions of n-paraffins in the oil fractions were determined by formation of an insoluble complex between the n-paraffins and urea (10). The uncomplexed oil was then treated with 35 volumes of acetone and chilled to -23°C (-10°F), whereby the branched paraffinic material was precipitated (11).

## Analytical Procedures

Gaseous materials were handled in a conventional glass vacuum apparatus equipped with storage reservoirs.

Gas-chromatographic analyses of the paraffinic fractions of the light oils were carried out with a 5751B F and M gas chromatograph equipped with a dual flame ionization detector. The chromatographic column was a 6-foot by 1/8-inch column loaded with 10% silicone rubber on 80-100 mesh Diatoport S. Gaseous mixtures were analysed at room temperature and for distillates the temperature was programmed to rise from 100°C to 280°C at the rate of 6°C per minute. Each analysis was carried out twice. Distillates were diluted with an equal volume of benzene. In each repeat analysis, samples of standard hydrocarbons were added to the mixture which enabled a more accurate determination of the peaks in the mixtures corresponding to known materials.

Proton magnetic resonance spectra were obtained using a Hitachi Perkin-Elmer R20 High Resolution NMR Spectrometer. All spectra were run using tetramethylsilane (TMS) as an internal standard. The samples were prepared as approximately 25%-by-volume solutions in spectroscopically pure carbon tetrachloride and the spectra were recorded immediately over the interval of 0-600 c.p.s. from TMS.

Mass spectra were recorded on a Perkin Elmer 270 Mass Spectrometer. Solids were introduced directly into the ionisation chamber whilst liquids were vapourised in vacuo into the ionisation chamber by preheating in a small oven.

Infrared spectra were recorded on a Perkin Elmer 221 Infrared Spectrometer; liquids were recorded as a film and solids at a concentration of 0.4% in potassium bromide.

## RESULTS

The aforegoing work shows that the asphaltenes can be cracked, under conditions similar to those employed for visbreaking (i.e. ~470°C) to afford a near aliphatic oil (H/C = 1.65) containing higher paraffins with lower molecular weight paraffins occurring as gases. There are marked similarities between products of the slow and rapid cracking processes with the interesting exceptions that the amount of light oil is increased significantly, yields of gases are reduced (Table I) and whilst paraffins are products of both cracking processes there are higher proportions of n-paraffins in the light oil from the slow distillation. In each case, reduction in hetero-atom content, occurring as water, hydrogen sulphide, and ammonia (traces), is especially noticeable in the oxygen analyses (Table II). This, and infrared spectroscopic evidence, indicates that whilst nitrogen and sulphur are not in dominant functional groups, and probably have thermal stability conferred upon them by incorporation into ring systems, the majority of the oxygen is located in thermally labile, e.g., carbonyl, groups. If this is indeed the case, the results may serve as a guide to illustrate the relative occurrence of the hetero-atoms in heterocyclic structures.

TABLE I   Destructive Distillation of Athabasca Asphaltenes

| Products | -- Distillation -- | |
| --- | --- | --- |
| | Rapid | Slow |
| Light oil (Yield, wt. %) | 35.2 | 43.9 |
| Resins (Yield, wt. %) | 4.5 | 4.5 |
| Coke (Yield, wt. %) | 48.4 | 49.0 |
| Gases | | |
| [wt. % (by difference)] | 11.9 | 2.6 |
| [wt. % (found)] | 11.2 | 2.3 |

TABLE II   Loss of Hetero-Elements during Cracking

| | ------ % (w/w) Loss ------ | |
| --- | --- | --- |
| | Rapid Heating | Slow Heating |
| Oxygen | 81.3 | 80.1 |
| Nitrogen | 1.0 | 1.0 |
| Sulphur | 23.4 | 17.1 |

Proton magnetic resonance and mass spectroscopy indicated an overall dealkylation of the aromatics to methyl (predominantly) and ethyl (minority) groups. There was also the indication that the predominant aromatics in the cracked products were based on the naphthalene nucleus. Other investigations showed that higher temperatures (>500°C) promote the formation of benzene, in place of naphthalene, nuclei as the predominant aromatics in the cracked material but this is accompanied by an increase in coke formation.

The formation of the paraffins can be ascribed to the generation of hydrogen within the system which occurs during the pyrolysis of condensed aromatic structures (12,13). Indeed, it (14) has been demonstrated that a surprisingly low amount of hydrogen is required to upgrade the Athabasca bitumen and other experiments by the present author with reduced* Athabasca asphaltenes show that increased yields of the lower molecular weight paraffins are produced during cracking of the hydrogenated asphaltenes. Thus, one of the major effects is a transfer of hydrogen within the system either by repeated condensation of aromatic material to coke or by complete aromatization of the naphthenes. The overall result is a highly saturated fraction – the light oil – and a highly condensed aromatic ring system – the coke.

Mass spectroscopic examination of the asphaltenes showed a whole range of fragmentation ions up to at least m/e 700. The particular fragmentation patterns will be discussed in detail in a later publication. However, more pertinent to the present work, there were several significant details which emerged from the spectra. There was a marked increase, with increasing temperature (from 60°C-350°C), of ions attributable to low molecular weight hydrocarbon fragments (m/e - 29, 43, 57, 71, 85), monocycloparaffins (m/e - 69, 83), alkylbenzenes (m/e - 91, 105), and naphthalenes (m/e - 125, 127, 141, 155). In fact, the mass spectra of the cracked products up to m/e 220 were very similar to the spectrum produced from the asphaltenes at 350°C. There is the suggestion here that the cracking processes involve predominant formation of fragments of the above types (presumably as free radicals) which then interact with the hydrogen produced to yield the end-products. Indeed, the identification of paraffins, methyl and, to a lesser extent, ethyl benzenes and naphthalenes among the products lends credence to this view.

The facile elimination of oxygen, predominantly as water, during cracking was confirmed in part by the intense peaks at m/e 17, 18 whilst sulphur elimination in elemental form or hydrogen sulphide was also confirmed by peaks at m/e - 32, 33, and 34. Peaks due to the elimination of nitrogen as ammonia were not so prominent but there was the suggestion of nitrogen occurring in pyridine nuclei and also sulphur in benzothiophene nuclei. This would confirm the postulate that these elements are not liberated as readily as oxygen during the cracking because of the stability conferred on them through location in ring-systems. In addition, the majority of nitrogen and sulphur remaining in the products occurs in the coke.

It is apparent from these results, that carbon-carbon bond fission occurring during thermal degradation of the asphaltenes is greatest at the bond β to an aromatic ring. Intramolecular condensation of the aromatic moieties yielding coke and generating hydrogen within the system are also dominant reactions. At present, it is not known whether the hydrogen so generated, and also by aromatisation of naphthene structures, exists as free hydrogen or merely participates in the processes in the form of an intramolecular hydrogen transfer.

In addition, the facile elimination of oxygen as water and, to a lesser extent, sulphur and nitrogen as hydrogen sulphide and ammonia, respectively, affords a convenient means of eliminating these elements from the products. It would appear, therefore, that high proportions of the sulphur and nitrogen originally present in the asphaltenes are located in ring-systems and are largely incorporated into the coke during cracking.

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* Using lithium metal/ethylenediamine or elemental hydrogen/catalyst or lithium aluminum hydride.

## ACKNOWLEDGEMENTS

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